

# Carbon isotope evidence for CO<sub>2</sub> dissolution and fluid-rock interaction at the Weyburn CO<sub>2</sub>-injection enhanced oil recovery site, Saskatchewan, Canada

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## Abstract

Geochemical and isotopic analyses of produced fluid at EnCana's Weyburn CO<sub>2</sub>-EOR operation are being used as a monitoring tool for fluid-rock reaction and injected CO<sub>2</sub> dissolution and distribution. Chemical parameters (e.g. pH and cation/anion concentrations) show dissolution of injected CO<sub>2</sub> and localized carbonate dissolution. These processes are best illustrated with evolving carbon isotope compositions of bicarbonate ( $\delta^{13}\text{C}_{\text{initial}} = -3\text{‰}$ ), reservoir minerals ( $\delta^{13}\text{C} = +4\text{‰}$ ), produced CO<sub>2</sub> ( $\delta^{13}\text{C}_{\text{initial}} = -13\text{‰}$ ), and injected CO<sub>2</sub> ( $\delta^{13}\text{C} = -34\text{‰}$ ). Localized calcite and dolomite reservoir dissolution results in higher  $\delta^{13}\text{C}$  values for aqueous bicarbonate. CO<sub>2</sub> dissolution dominates near high volume CO<sub>2</sub> injectors, where injected CO<sub>2</sub> with low  $\delta^{13}\text{C}$  values has been traced into produced fluid.

## Introduction

The Weyburn field is one of a number of large oilfields that lie along the Mississippian subcrop belt on the northern extent of the Williston Basin. The Weyburn field is located approximately 130 kilometers southeast of Regina, Saskatchewan, Canada (Figure 1) where medium gravity crude oil is produced from the Midale beds [1] of the Mississippian Charles Formation. This reservoir is comprised of the low permeability dolomitic Marly zone and the underlying calcitic, more permeable, Vuggy Shoal and less permeable Vuggy Intershoal zones. Oil-bearing reservoir rocks are overlain by an anhydrite cap.

The Midale beds of the Weyburn field were discovered in 1954 and produced by primary depletion until 1964, when injection of water was used to enhance oil recovery [1]. By 1996, cumulative production reached 328 million barrels of oil or 23% of the 1.4 billion barrels of the original oil-in-place. In 1997, PanCanadian (now EnCana Corporation) announced the Weyburn CO<sub>2</sub> miscible flood project, which is forecasted to add incremental oil recovery of 120 to 140 million barrels. The CO<sub>2</sub> used in the miscible flood originates from the Great Plains Synfuel coal gasification plant in Beulah, North Dakota by way of a 320-kilometer pipeline (Figure 1). CO<sub>2</sub> and water are injected into the reservoir over a 19-spot pattern (Figure 1).

### *Miscible CO<sub>2</sub> flooding*

Under the correct conditions of pressure, temperature and oil composition, CO<sub>2</sub> becomes miscible with oil and causes the residual oil to swell, lowering the viscosity. CO<sub>2</sub> is injected with water to retard CO<sub>2</sub> mobility. A factor thought to increase oil recovery during CO<sub>2</sub> injection is the increase in permeability due to the acidity of carbon dioxide-water mixtures. Acid gases have been suggested to dissolve carbonate minerals in the formation matrix resulting in a permeability increase [3].

## CO<sub>2</sub> and Carbonate Mineral Dissolution

Carbonate reservoirs typically containing Fe-, Mg- and Ca-bearing carbonates have low trapping potential for CO<sub>2</sub> as can be shown by the reactions:

- (1) CO<sub>2</sub> dissolution:  $\text{H}_2\text{O} + \text{CO}_2 \rightleftharpoons \text{H}_2\text{CO}_3^* \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$
- (2) Calcite dissolution:  $\text{H}^+ + \text{CaCO}_3 \rightleftharpoons \text{Ca}^{2+} + \text{HCO}_3^-$
- (3) Both CO<sub>2</sub> and calcite diss<sup>n</sup>:  $\text{H}_2\text{O} + \text{CO}_2 + \text{CaCO}_3 \rightleftharpoons \text{Ca}^{2+} + 2\text{HCO}_3^-$

Reaction (1) represents CO<sub>2</sub> dissolution, and results in the modified fluid having a lower pH and higher [HCO<sub>3</sub><sup>-</sup>]. Reaction (2) represents reservoir calcite dissolution. This reaction leads to higher carbonate alkalinity and higher cation concentrations. If both reactions take place, as shown by reaction (3), then for each mole of injected CO<sub>2</sub> that reacts, we can expect one mole of cation, and 2 moles of HCO<sub>3</sub><sup>-</sup> dissolved in the *in situ* fluid.

Injected CO<sub>2</sub> has a very low  $\delta^{13}\text{C}$  value (-34‰ V-PDB) that can be traced via the reactions above into bicarbonate and produced CO<sub>2</sub> at the wellhead (reactions 1 and 3). Dissolution of relatively  $\delta^{13}\text{C}$  enriched carbonate minerals (without input of injected CO<sub>2</sub>) leads to an increase of  $\delta^{13}\text{C}$  values of produced bicarbonate and CO<sub>2</sub> (reaction 2)

## Results

### *Aqueous geochemistry*

Selected geochemical and isotopic parameters are plotted as contoured maps in Figures 2, 3, and 4. In Figure 2, total alkalinity has increased up to three fold over the first two years of CO<sub>2</sub> injection. Similarly, Ca concentrations have doubled in some zones of the injection pilot area. These increases are consistent with the reactions (2) and (3) above, the dissolution of reservoir minerals. Figure 3 contour maps show the approximate distribution and volume of injected CO<sub>2</sub>, and the measured pH. Lows in pH and highs in alkalinity and Ca are spatially consistent with the zone of highest CO<sub>2</sub> injection volumes. The drop in measured pH and corresponding increases in alkalinity are consistent with reaction (1) above, the dissolution of injected CO<sub>2</sub>.

### *Carbon isotope geochemistry*

Carbon isotope signatures of fluid, gas, and minerals at Weyburn are distinct. Reactions involving dissolution of injected CO<sub>2</sub> and carbonate minerals can be traced in the resulting produced fluid and gas. Injection CO<sub>2</sub> has a  $\delta^{13}\text{C}$  value of -34‰, while calcite and dolomite have  $\delta^{13}\text{C}$  values between 2.8 and 5.5‰. Baseline (pre-injection) dissolved CO<sub>2</sub> in the reservoir fluid (HCO<sub>3</sub>) and produced CO<sub>2</sub> gas have carbon isotopic signatures of -2.8‰ and -12.7‰, respectively.

Reactions (1) and (2) should have a profound effect on the carbon isotope results. With injected CO<sub>2</sub> dissolution (Reaction 1), the CO<sub>2</sub> from Beulah, which is depleted in <sup>13</sup>C, will be reflected in isotopically lighter produced CO<sub>2</sub> and HCO<sub>3</sub> (i.e. more negative values). Alternatively, with carbonate mineral dissolution (Reaction 2), produced CO<sub>2</sub> and HCO<sub>3</sub> will be enriched in <sup>13</sup>C (i.e. more positive values). Figure 4 shows the initial NW-SE field-wide variation in isotopic values. After 289 days of injection, sharp decreases are evident in the southeastern portion of the pilot area and correspond with the highest injected CO<sub>2</sub> volumes. After 644 days of injection bicarbonate <sup>13</sup>C data show some slight increases in  $\delta^{13}\text{C}$  values from the previous year. The zones of slight  $\delta^{13}\text{C}$  increases are spatially consistent with high Ca concentrations.

The preliminary  $\delta^{13}\text{C}$  data suggest that  $\text{CO}_2$  dissolution was the dominant process during the first year of  $\text{CO}_2$  injection. By the second year, calcite and dolomite dissolution have contributed to the changing water and gas chemistry. The data therefore suggest that both  $\text{CO}_2$  dissolution and carbonate mineral dissolution took place during the first 22 months of  $\text{CO}_2$  injection. Mass balance calculations in the near future will help quantify the respective inputs of each dissolution process on the resulting water and gas chemistry.

## Summary

The trends in chemical composition and the isotope data suggest that the reaction of injected  $\text{CO}_2$  with the formation water lowered pH, resulting in dissolution of carbonate minerals and production of bicarbonate. Mineral dissolution raised the pH and production of bicarbonate. These reactions result in storage of injected  $\text{CO}_2$  in the formation water as bicarbonate ions. The southern and southeastern injection wells have the highest cumulative  $\text{CO}_2$  injection volumes. These areas coincide with high alkalinity, low  $\delta^{13}\text{C}$  values in the bicarbonate phase, and lower pH. These trends point towards dissolution of injected  $\text{CO}_2$  ( $\delta^{13}\text{C}_{\text{CO}_2} \sim -34\text{‰}$ ) in the reservoir fluid. Increases in Ca concentration, alkalinity,  $\delta^{13}\text{C}(\text{HCO}_3^-)$ , and pH together are indicative of carbonate dissolution.

## References

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- [2] Burrowes, G. and Gilboy, C. Investigating Sequestration Potential of Carbonate Rocks During Tertiary Recovery from a Billion Barrel Oil Field, Weyburn, Saskatchewan: The Geoscience Framework. IEA Weyburn  $\text{CO}_2$  Monitoring and Storage Project Report. 2000:
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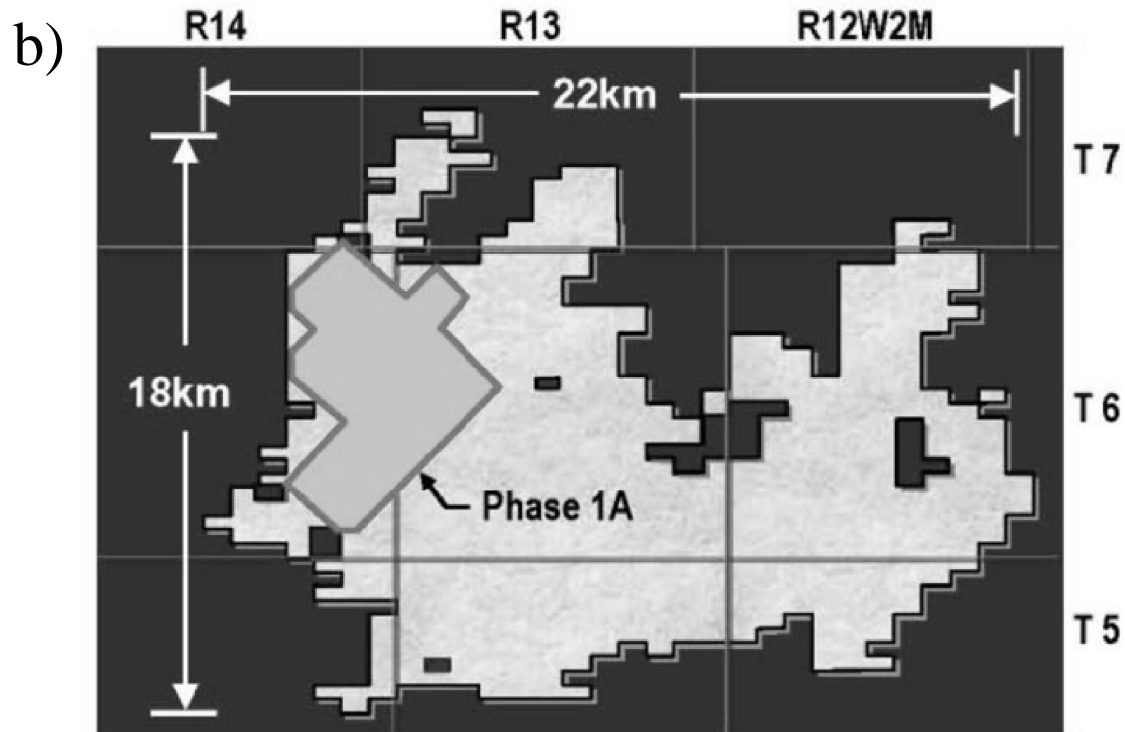
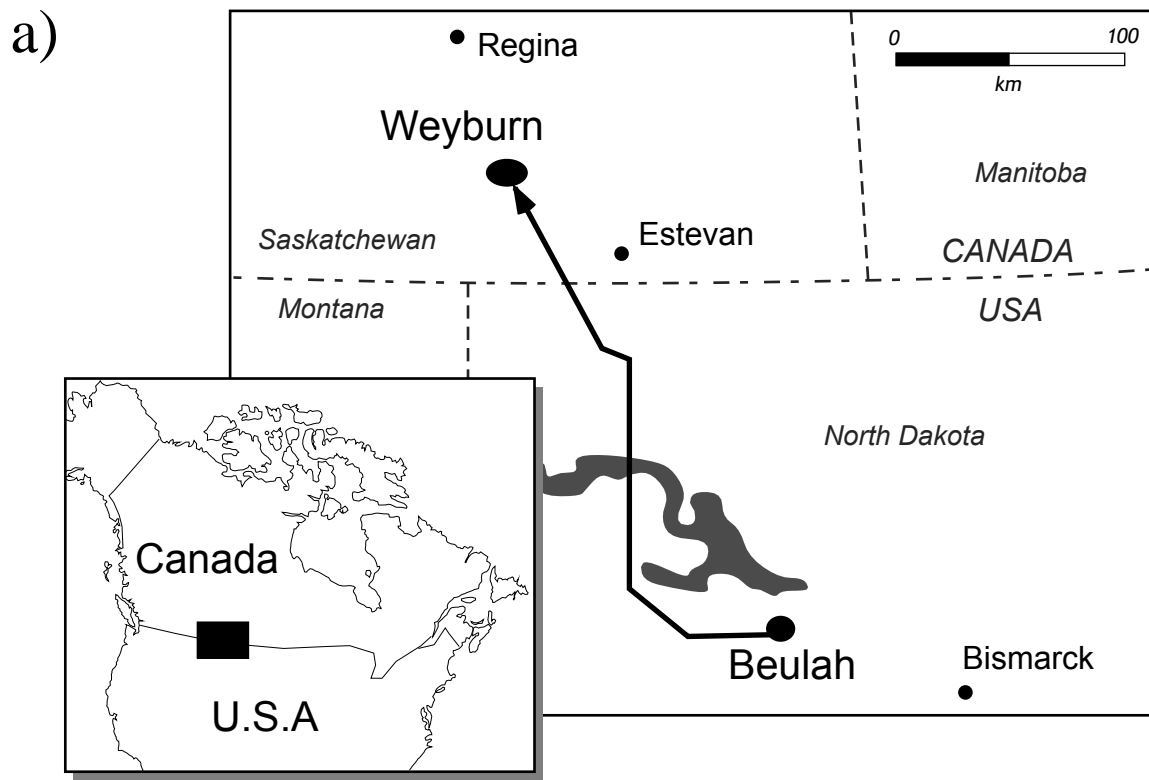
## Figure Captions

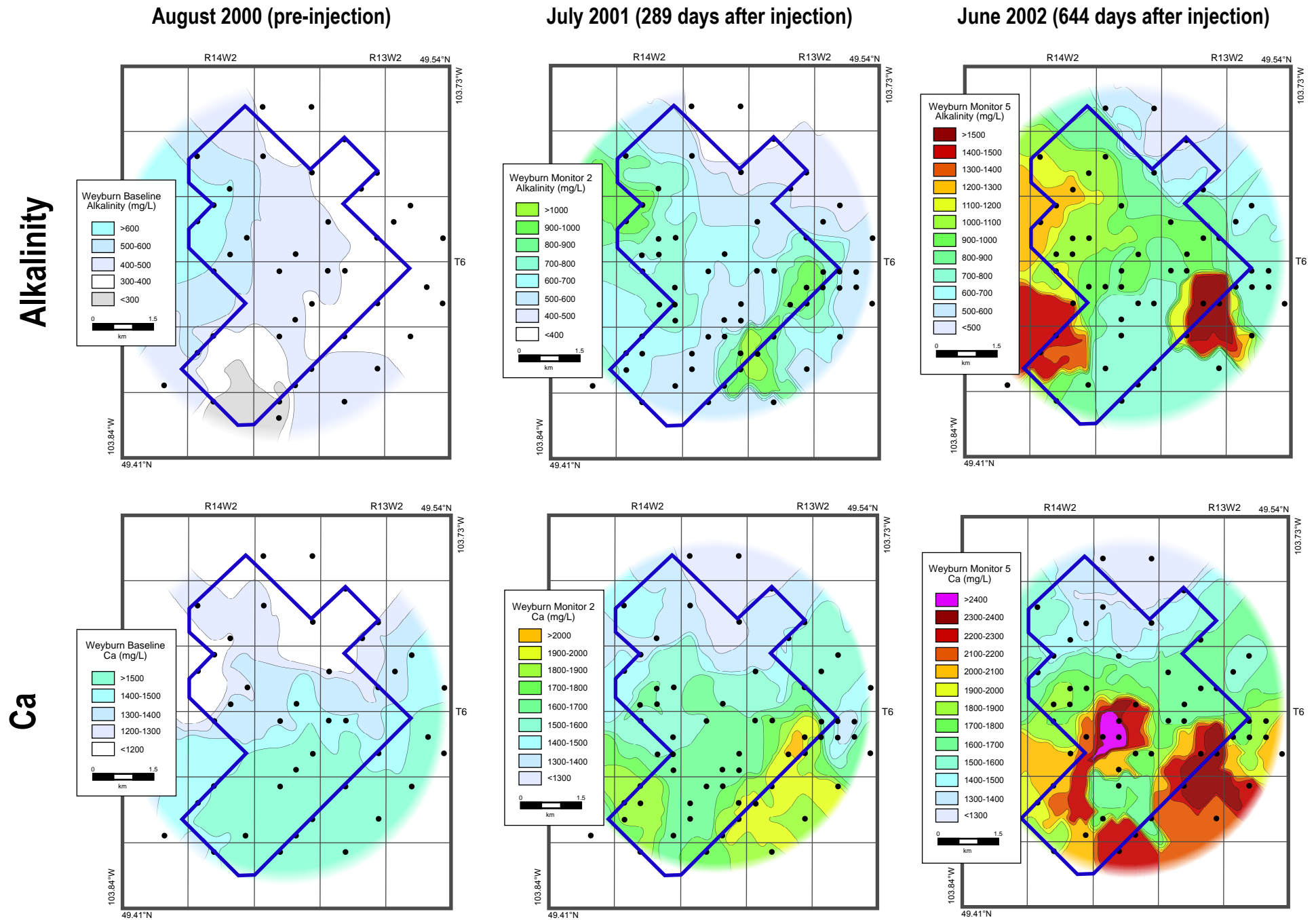
Figure 1: a) Location of the Weyburn field. The map on the left shows the approximate location of the  $\text{CO}_2$  pipeline from Beulah, North Dakota. b) Location of the Phase 1A pilot injection area within the Weyburn oil field. The Phase 1A injection area is highlighted on contour maps in Figures 2 and 3 (after [2]).

Figure 2: Contour maps of total alkalinity (mg/L) and  $\text{Ca}^{2+}$  concentration (mg/L) in produced fluid for the pilot injection area. The black dots represent sampling points at depth in the reservoir. Note the increased alkalinity and Ca concentration as  $\text{CO}_2$  injection progressed.

Figure 3: Contour maps of injected  $\text{CO}_2$  volumes (thousand standard cubic metres) and measured pH for the pilot injection area. For the  $\text{CO}_2$  injection contour maps, dots represent the locations of vertical and horizontal (midpoint) injectors.

Figure 4: Contour maps of  $\delta^{13}\text{C}$  in bicarbonate from produced fluid and  $\text{CO}_2$  from produced gas in the Phase 1A pilot injection area. Note general decreases in  $\delta^{13}\text{C}$  values after injection. By June 2002, increases in  $\delta^{13}\text{C}$  in bicarbonate can be seen, possibly a result of carbonate mineral dissolution.





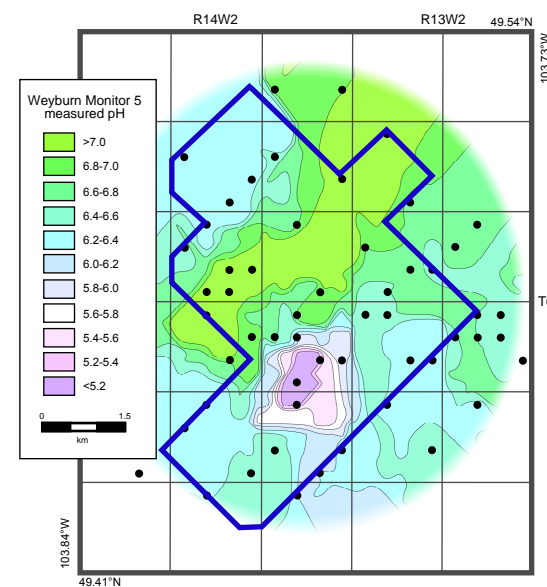
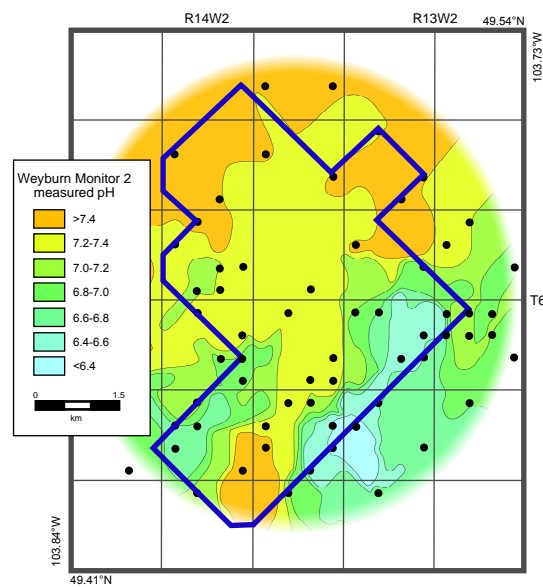
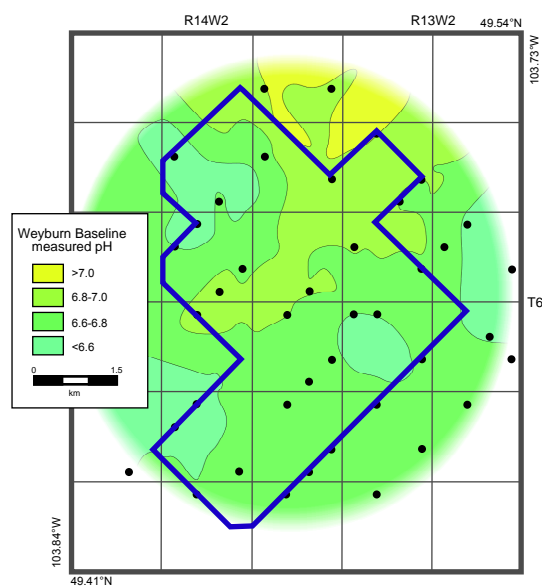
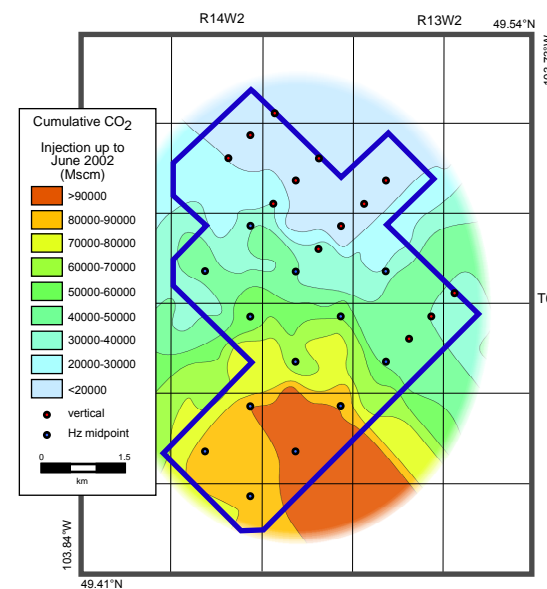
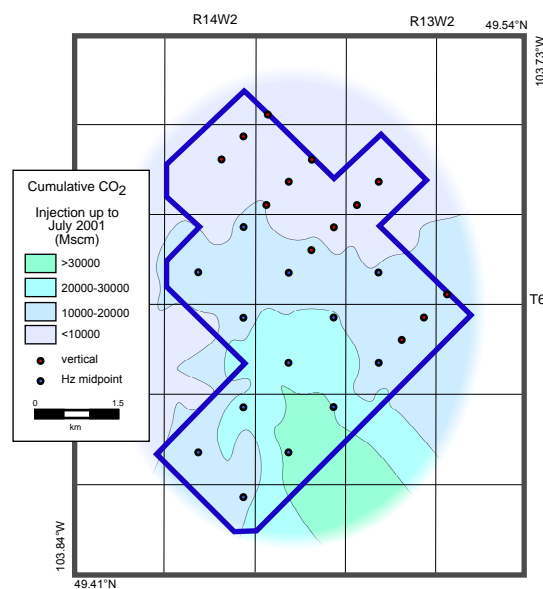
Injected CO<sub>2</sub>

August 2000 (pre-injection)

July 2001 (289 days after injection)

June 2002 (644 days after injection)

Prior to CO<sub>2</sub>  
Injection



pH

